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Alarm-Level Monitor for SO2 Emissions from Stationary Sources

International Biophysics Corp, Irvine, Calif

Prepared for

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Environmental Protection Technology Series

ALARM-LEVEL MONITOR FOR [illegible] EMISSIONS FROM STATIONARY SOURCES

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16 ABSTRACT

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ALARM-LEVEL MONITOR FOR SO_2 EMISSIONS FROM STATIONARY SOURCES

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SECTION 1

INTRODUCTION

EPA regulations require that all new and modified stationary sources be equipped and monitored for specific pollutants emitted from specified categories of sources. The applicable monitoring systems must be capable of quantitatively detecting the pollutant gases of interest and generating and recording emission data continuously as a function of time. There are presently available several commercial monitoring systems to meet these needs. Generally, these monitoring systems are complex in design and require skilled personnel for set up, calibration, and operation. Thus, by nature, such monitoring systems are expensive to purchase ($20,000-$50,000) as well as costly to maintain. These costs are considered reasonable for new and substantially modified sources.

However, existing sources outnumber new and modified sources. These existing unmodified sources are regulated by State Implementation Plans, which usually encompass legal limits on emissions. Some states now require monitoring of emissions from existing individual sources and it is anticipated that similar requirements will be imposed for additional sources.

A large number of the existing source facilities are small in size, production-wise, and do not normally employ the type of skilled personnel needed to maintain complex monitoring systems. It would be prohibitive, from a cost and practical standpoint, to require monitoring these sources with present commercially available systems.

Additionally, there are many existing sources in which the type of operation involved does not necessitate the generation of emission data on a continuous basis. Because of the nature of the emissions (high concentrations for short periods and low concentrations for longer period), continuous monitoring and data collection is highly impractical. An alternate approach would be to detect those instances when specified emission limits are exceeded. An Alarm-type monitoring system will achieve essentially the same control as the more complex systems but with the inherent advantages of being simpler in design and operation, requiring a minimum of data collection and analysis, and thus less costly to purchase and maintain.

The purpose of this contract was to develop a field prototype, alarm-level monitor for sulfur-dioxide (SO_2) emissions from stationary sources. The system design was to be as simple and straightforward as practical and such that future commercial production of the system is possible.

SECTION 2

SUMMARY

A field prototype alarm-level monitor for SO_2 emissions from stationary sources was designed, developed, fabricated and field tested under this contract.

Design criteria for the monitor resulted from a parametric study of all factors impacting a specific monitoring concept--that concept being that small, unsophisticated, existing source facilities faced with meeting local legal limits on emissions need an inexpensive monitor that requires minimum instrument maintenance. The parametric study considered the following:

- a general industry emission study to identify potential instrument users and obtain an overview of typical effluent composition, effluent levels, and source monitoring operating practice.

- a study of applicable regulatory guidelines and standards for SO_2 source emissions to determine the required instrument concentration level capability.

- general operator skill level, industrial procedures, servicing and maintenance requirements and reliability under field service conditions.

- SO_2 measuring concepts, and potential manufacturing cost reductions through design simplification.

Results of the study were as follows:

- An electrochemical transducer type SO_2 sensor most closely matched the criteria.

- Analyzer sensitivity from 100-1000 ppm would meet the vast majority of field applications.

- Visual and acoustical signaling devices activated when preselected adjustable emission levels have been reached is adequate operator alarm.

- Measurement accuracy of ± 20% relative to EPA Method No. 6 is adequate for this usage.

- System response time should be 10 minutes or less.

- Every effort should be made in the design to incorporate plug-in component modules, roomy instrument cabinets, etc., for easy maintenance.

An electrochemical analyser complete with refrigerated sample dryer, heat trace sample line and sample probe was developed and tested. The tests, performed on the scrubber section of a light weight aggregate rotary kiln process, indicated the design performance goals are met by the analyser.

A cost analysis of the monitoring system indicated that the system may be marketed at a cost below $2,500 excluding the probe assembly.

SECTION 3

CONCLUSIONS

A source monitoring system was developed under this contract for visual and audible alarm when SO_2 emission exceeds a predetermined level. The results of the field tests of this system are presented below.

(1) The nature of the process plant chosen for field test was such that the hot gas exhaust section had an exceedingly high particulate loading which plugged the sample probe almost immediately. Measurements were then taken on the downstream side of a wet scrubber. The gas at this point was cool and the particulate level was reduced but the sample was saturated with water vapor. This water vapor condensed in the unheated probe and backflushing was required from time to time to prevent blockage.

In by far the majority of sources which use this instrument, the gas will be much hotter, the probe temperature will be higher and the water vapor condensation should not be a problem. The sample line also may be backflushed if the probe filter becomes loaded with particulates, using the high pressure auxiliary air supply.

(2) The system calibration concept called for a pressure operated check valve in the probe to allow span gas to be introduced at the probe, thus providing a true 'system' calibration. Unfortunately, in the field test the stack gas was cool as well as the probe and check valve thus preventing the check valve from seating and sealing properly on a Teflon seat. The calibration concept seems correct, however, further testing at hotter temperatures is needed.

(3) The new electrochemical cell developed for the analyzer functioned well. Improved features such as the large electrolyte reservoir for long operating life and the elimination of temperature conditioning on the cell cannot be properly judged without long term testing which was not possible in this program.

(4) Wherever the sample probe or stack fittings are exposed to a gas flow with high water vapor, 316 stainless steel should be used rather than 304 to reduce corrosion of the metal.

(5) The cyclic concentration component observed in some of the analyser data could not be traced to either a plant performance parameter or to the analyzer. Further tests are needed to fully establish analyser performance.

(6) The field test, which compared the new analyser concentration measurement on a strip chart to an EPA Method 6 measurement on side-by-side sampling resulted in an analyser relative accuracy of 16.7%.

SECTION 4

SO_2 MONITOR SYSTEM DESCRIPTION

The instrument system developed under this contract is an extractive type that employs a probe assembly for taking a gas sample from any selected location in a stack, flue or process stream. Principle elements of the system are illustrated schematically in Figure 1. A check valve located near the probe tip provides a method of introducing span gas for true system calibration by passing the calibration gas through every element of the instrument system. A filter also located in the probe line removes any solid particulates such as fly-ash from the sample. The sample gas flows from the probe to the instrument cabinet, shown in Figure 2, through heat-traced line to prevent water vapor condensation and consequent SO_2 loss by absorption in the water. The sample passes through a heat exchanger coil which is cooled by a reliable, low cost refrigeration unit. The gas sample stream along with any water which is condensed out of the gas stream at the end of the heat exchanger, enters a separator section wherein a portion of the dried gas sample is continuously extracted for SO_2 analysis.

The total probe gas sample is pulled through the system, including the separator, by means of an air operated high volume flow aspirator. The high volume sample flow results in a short residuence time for the SO_2 in the gas stream with the separator's condensed water. The low volume flow dry gas sample is drawn from the separator by a separate vacuum pump, passes through a flowrator and final particulate filter and enters the SO_2 analyzer cell.

The analyzer contains an electrochemical membrane polarographic type cartridge sensor. The sensor distinguishes the SO_2 gas from other components in the gas stream and produces an electric current by electro-catalytic oxidation which is directly proportional to the SO_2 concentration. The concentration is indicated on an analog meter and the signal is available as a recorder output.

The analyzer is calibrated using 'zero' gas as supplied by atmospheric air which has been scrubbed of SO_2 and by means of calibration span gas of known concentration introduced either at the monitor cabinet or at the probe itself.

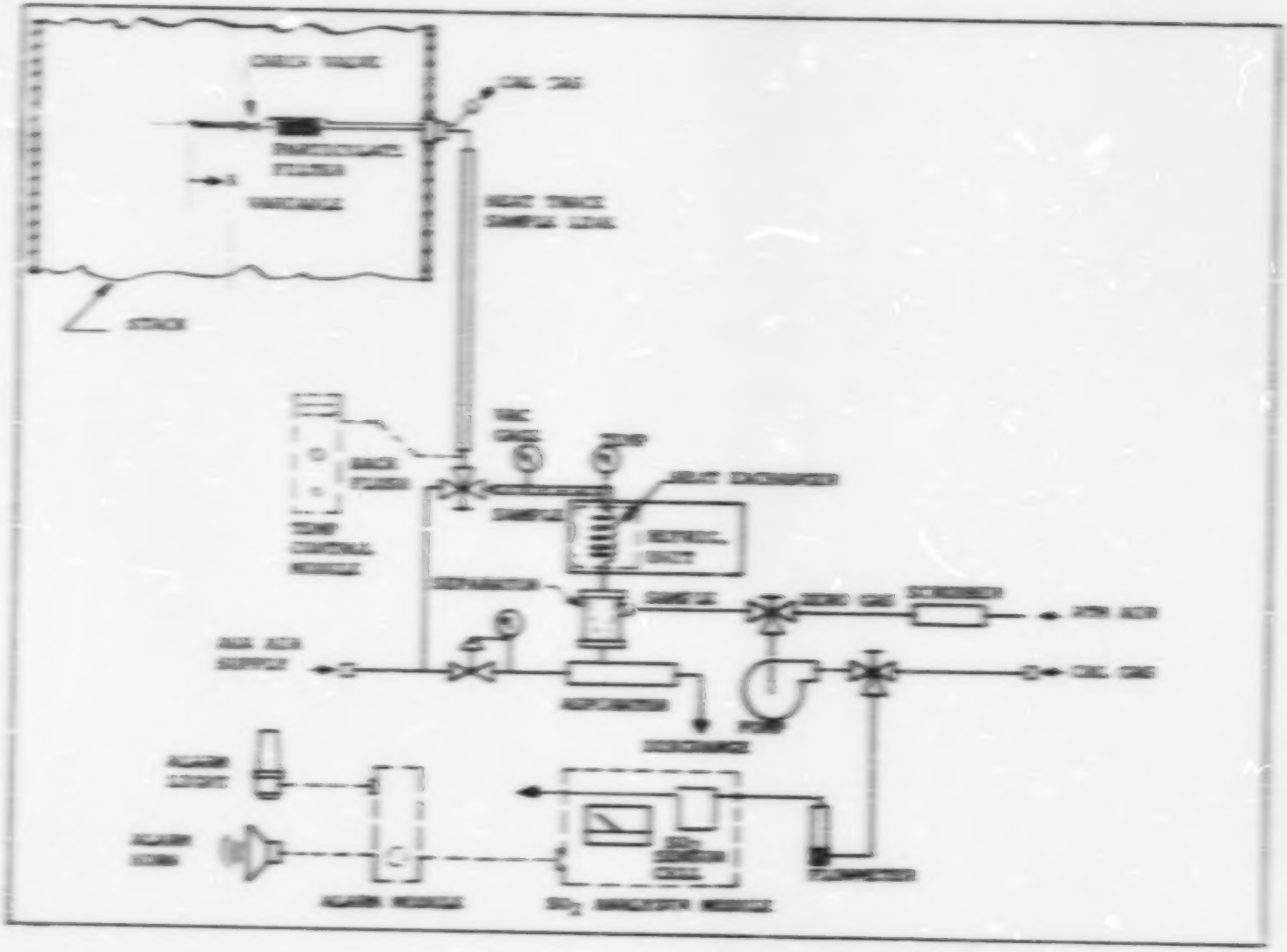


FIGURE 1. SO_2 MONITOR SYSTEM.

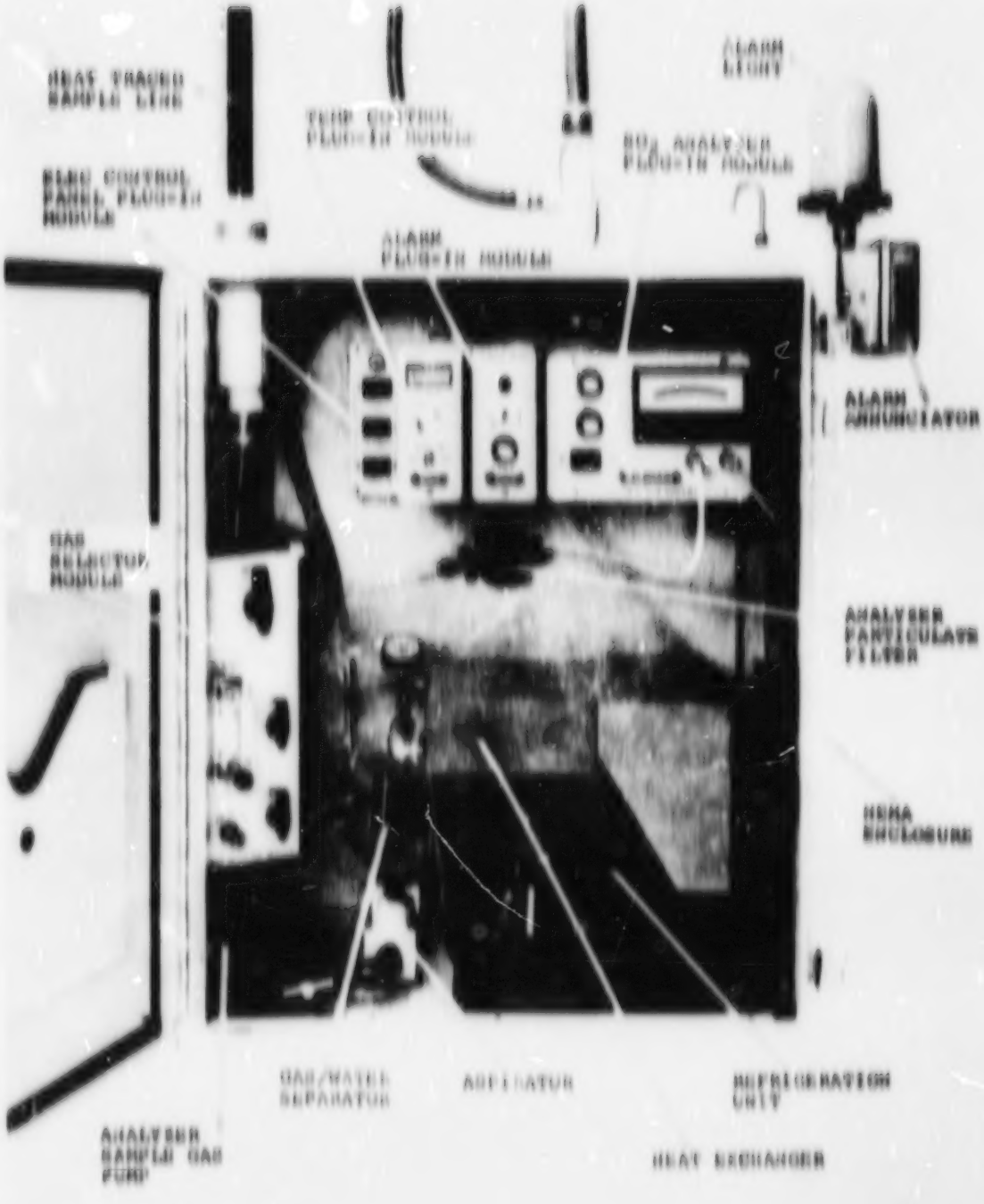


FIGURE 3. SO_2 MONITOR INSTRUMENT CABINET.

An alarm module is adjustable to any desired SO_2 concentration level. SO_2 levels above this preselected level are indicated both by activation of an annunciator and by an external light.

The sample line may be backflushed if the probe filter becomes loaded with particulates, using the high pressure auxiliary air supply.

The monitoring system, with the exception of the probe and sample line, is housed in a NEMA enclosure for rugged external environment protection. The system is conveniently broken down into subsystems which are designed as individual plug-in modules to expedite removal by nontechnical personnel at the field site. The subsytems include the following:

a) Analyser Plug-in Module.

b) Temperature Control Plug-in Module.

c) Alarm Plug-in Module.

d) Electrical Control Panel Plug-in Module.

e) Gas Handling Panel.

f) Refrigeration/Heat Exchanger Unit.

Each of these subsystems can be easily removed for factory maintenance. The selected NEMA enclosure is purposely large and roomy to ease maintenance.

System's performance specifications are shown in Table 1.

TABLE 1. SYSTEM SPECIFICATIONS

Range:	0-1000 ppm Direct reading in parts per million by volume. Span has 300% over range capability.
Accuracy:	System- ± 20% of f.s. max. accumulated error for 24 hours. Analyser- ±2% of f.s. referenced to span gas
Repeatability:	±1% of f.s.
Minimum Detectability:	±1% of f.s.
Linearity:	±1% of f.s.
Span Drift:	±1% of f.s. (4 hrs) ±2% of f.s. (24 hrs)
Electronic Drift:	±1% of f.s. per 24 hrs.
Response Time:	30 sec max to 95% of f.s.
Ambient Operating Temp:	10-110 °F
Power:	115 Vac, 60 Hz, 800 watt

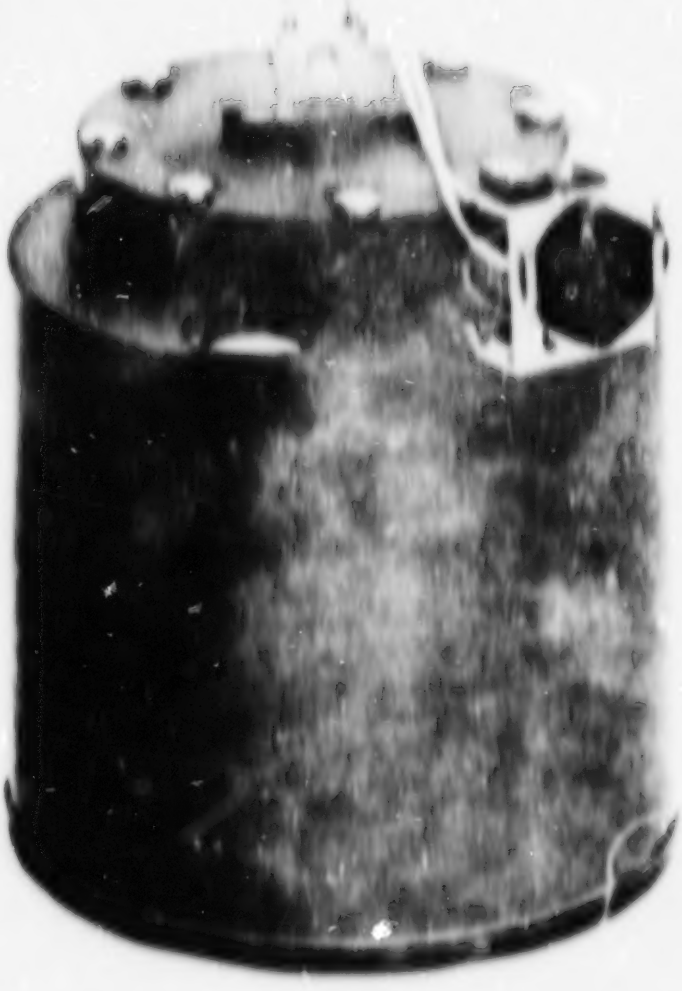
SECTION 5

SO_2 SENSOR OPERATING PRINCIPLE

The SO_2 sensor, located in the analyser, belongs to the category of electrochemical membrane-type polarographic gas detectors. The gas sample flows across the sensor membrane during gas stream passage between inlet and outlet parts. Some of the gas molecules diffuse through the membrane and dissolve in a thin liquid film at the sensing electrode surface where they are absorbed and undergo electroxidation or reduction. The opposite reaction occurs at a reference electrode resulting in electron current flow in the load circuit. A separating matrix insulates the sensing and reference electrodes and serves as an ionic conductor to maintain electro-neutrality. Spare electrolyte is contained in a reservoir in a bound state and maintains contact with the matrix through capillary action. The sensor unit is shown in Figure 3.

Sensor Selectivity

Sensor selectivity is based on the standard electrode potential of the electrochemical reaction involving the gas being measured. By controlling the potentials at which the electrode reactions occur, reactions of certain interfering gases can be minimized, thereby removing them as interferences. With the SO_2 sensor biased to maximise SO_2 response the interference equivalents for other possible gas constituents is given in Table 2 as determined by tests reported in Reference 1.



GAS
SAMPLE
FLOW

FIGURE 3. ELECTRO CHEMICAL SO_2 GAS SENSOR.

TABLE 2. INTERFERENCE EQUIVALENTS

Interferent Gas	Equivalent Ratio
H_2S	25:1
O_3	~0.3:1
O_2	1000:1
NO	100:1
NO_2	~0.6:1
CO	100:1
He	100:1
CO_2	1000:1
H_2	1000:0

Reference[1]

"Evaluation of Portable Sulfur Dioxide Meters."

Contract No. HSM-99-73-1 (T.O. No. 2) for National Institute for Occupational Safety and Health, by Research Triangle Institute, Research Triangle Park, North Carolina 27709.

SECTION 6

LABORATORY TESTS

Long term zero drift and span drift tests were performed to check sensor cell performance. A sixty-four (64) hour unattended test was performed in the laboratory using 444 ppm SO_2 span gas and a programmable timer set on a 10% duty cycle i.e., one minute of sample gas and nine minutes of zero gas. Portions of the chart record are shown in Figure 4. The zero drift for the 64 hour period is observed to be essentially zero.

The span drifted from 444 ppm to approximately 495 ppm (11.5%) in the first eight (8) hours of operation while the sensor cell was reaching equilibrium. For the remaining 56 hours of test the span remained constant with 5 ppm maximum variation.

SECTION 7

FIELD TESTS

Field tests of the SO_2 Alarm Monitor were performed during the month of May 1976 at the Crestlite Corporation's light weight aggregate plant in San Clemente, California. The aggregate is produced continuously in a rotary kiln. Exhaust from kiln contains both large and fine particulate as well as sulfur compounds released from heated clay. The bulk of the large particulate is removed by a series of cyclone separators and a wet scrubber removes a significant portion of the fine particulate from the gas stream.

The field tests were intended to demonstrate the overall operational capability of the monitoring system in a field application and specifically to determine the system SO_2 measuring accuracy. The accuracy determination was accomplished by comparing the integrated real time SO_2 concentration reading of the monitoring system to the sample concentration obtained by the standard EPA method 6. This side by side sampling was performed at the downstream end of the wet scrubber as shown in Figure 5.

Testing was first attempted at the hot (500°F gas temperature) upstream end of the wet scrubber, however, the high particulate load plugged the sampling probe almost immediately. Testing was accomplished then on the downstream end of the scrubber where the gas stream particulate concentration was significantly reduced. The gas temperature was very low in the scrubber exhaust resulting in partial condensation of the saturated water vapor. The sampling probe was pointed downstream to prevent excessive entertainment of water mist into the sample gas stream. The low gas temperature, however, meant a low probe temperature with some water vapor condensation prior to the heated sample line. Frequent backflushing was required to prevent flow restriction during the one hour test period. The Teflon seat in the probe check valve requires an elevated temperature in order to seal properly with back pressure. With the probe at the low temperature of the exhaust stack gas, the system calibration from probe on through to analyzer could not be performed because of the check valve leakage. Calibration thus was performed at the analyzer for these field tests.

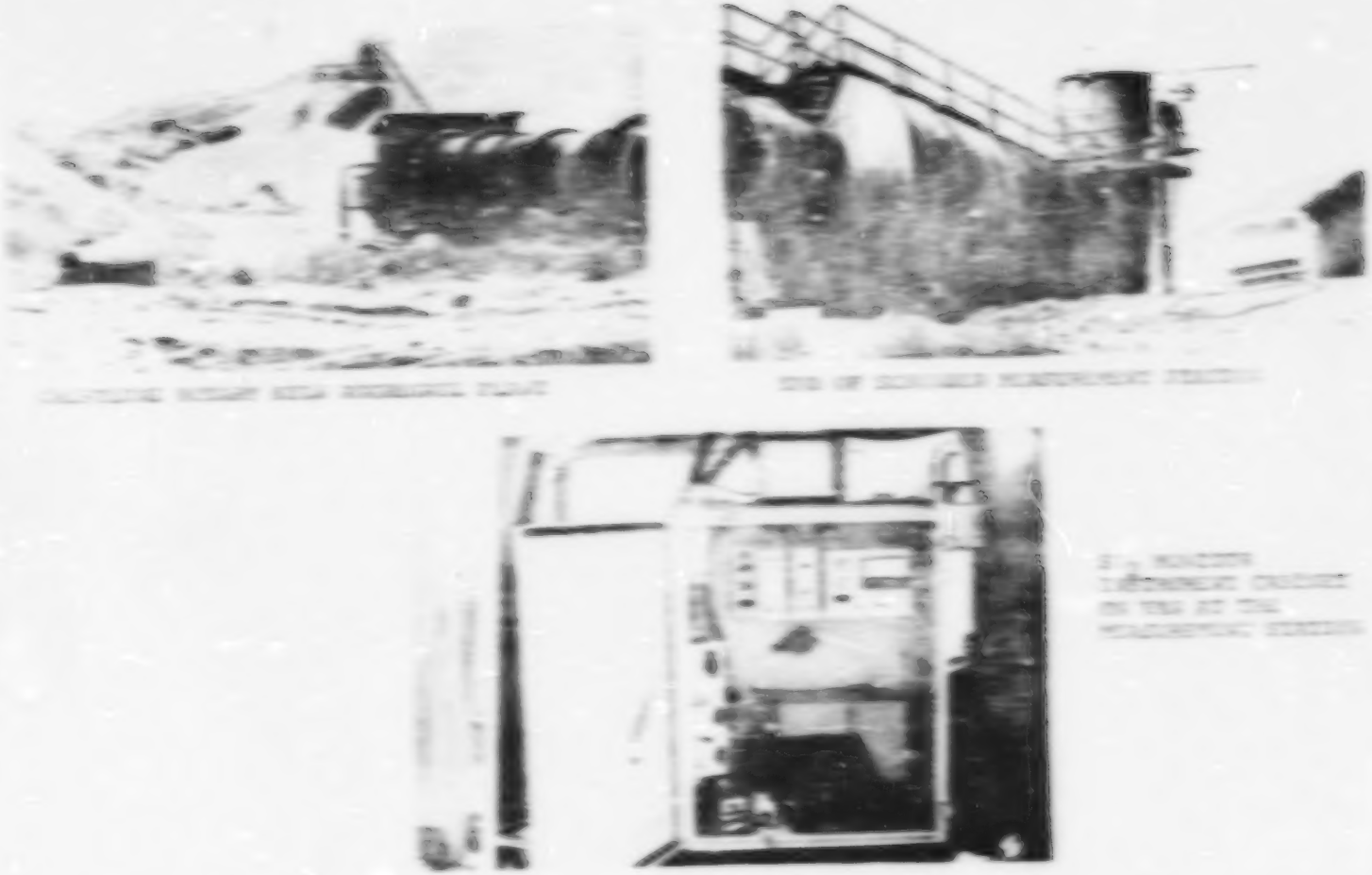


FIGURE 1. SO_2 MONITOR FIELD TEST SETUP.

Test Procedure

The system was backflushed and the analyzer zeroed and spaned with 430 ppm span gas prior to each run. A strip chart record was made of the analyzer output at the same time the sample was being taken with the sampling train. All sampling with the standard sampling train was done in accordance with EPA method 6 procedures. These samples were analyzed by an independent laboratory, Analytical Research Laboratories Inc. of Monrovia, California, and compared with the integrated strip chart record.

Test Results

The summarized results of eight tests are given in Table 3 and the pertinent data from the sampling train tests in Appendix A. The strip chart records from the SO_2 analyzer are presented in Figure 6.

The comparative results indicate the SO_2 Alarm Monitor is well within the ±20% accuracy design goal (with the exception of one test point) assuming the sampling train test results are accurate.

The cause of the cyclic analyzer signal in Run 2 and part of Run 3 could not be traced to the analyzer which responded normally during span gas calibration nor to any cyclic plant process phenomena. Likewise, backflushing failed to eliminate the phenomena. Further field tests are needed to achieve a high level of reliability in the instrument.

TABLE 3. ANALYZER ACCURACY DETERMINATION

Test No.	Date & Time	Reference Method Samples SO_2 - ppm	Analyzer I-Br* SO_2 Average-ppm	Difference Continuous Ref.--ppm
1	5/10/76 10:00	372	328	-44
2	5/12/76 9:02	276	206	-70
3	5/12/76 10:00	242	241	-1
4	5/12/76 11:00	223	203	-20
5	5/12/76 12:00	174	193	+15
6	5/12/76 13:00	221	238	+17
7	5/12/76 14:00	262	253	-9
8	5/12/76 15:00	328	300	-28

Mean Reference Method Test Value = 262.25

Mean Differences = 26

95% Confidence Intervals = $\pm$17.77

$$\text{Accuracy} = \frac{26 \pm 17.77}{262.25} = 16.7\%$$

*Analyzer average obtained by integrating strip chart records.

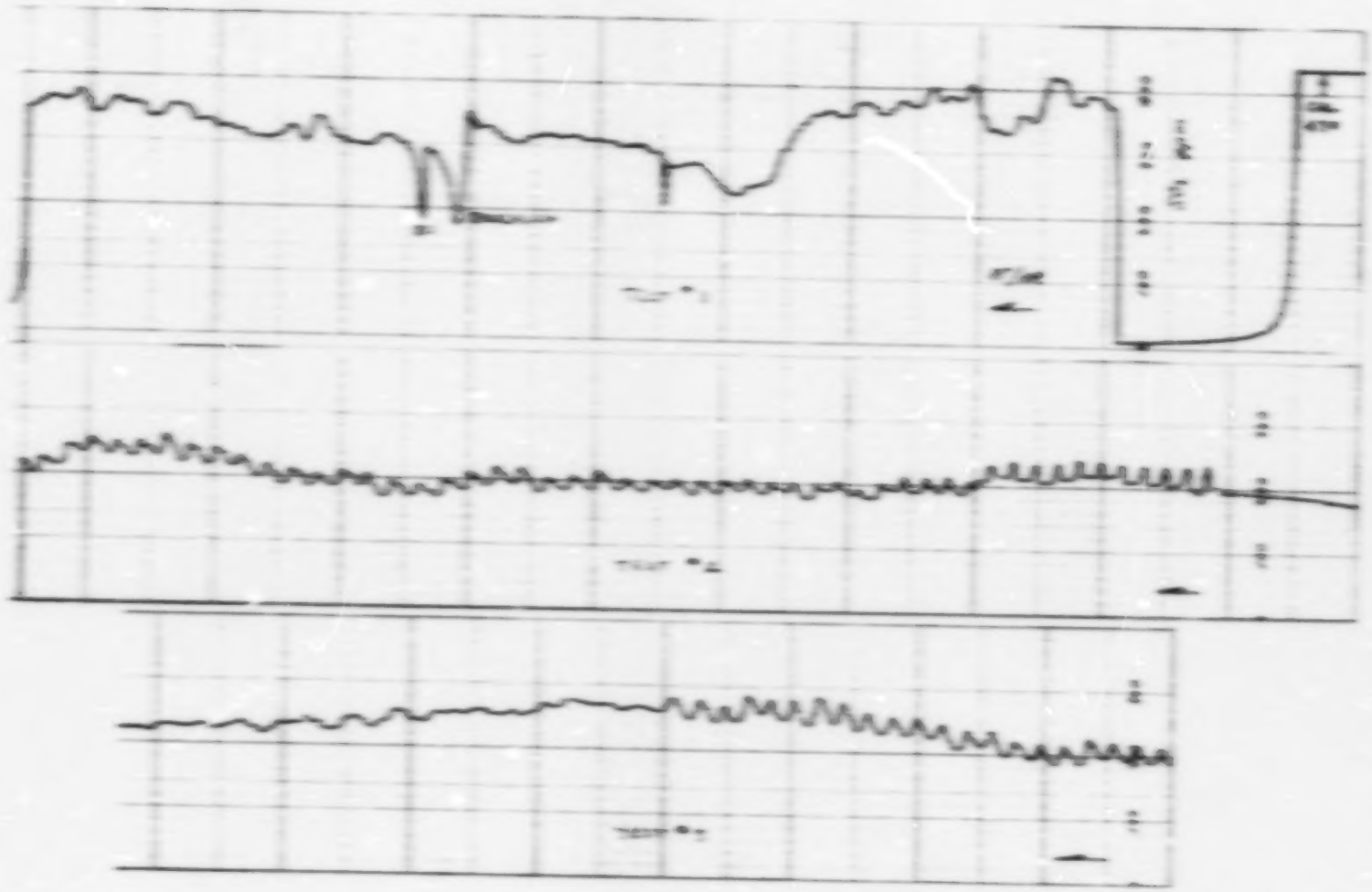


FIGURE 4a. FIELD TEST CHART RECORDS.

FIGURE 6. FIELD TEST CHAIR RECORDS.

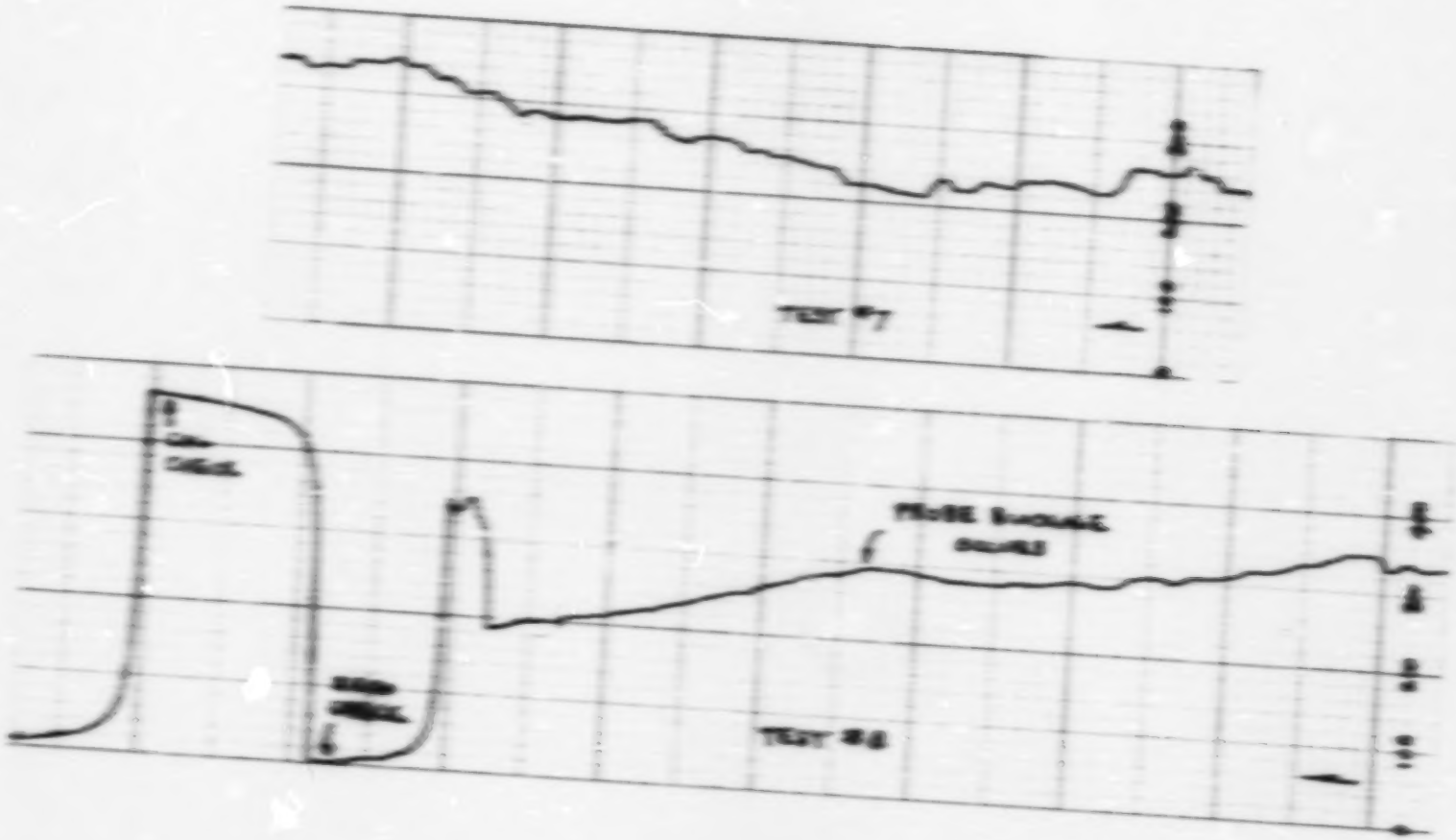


FIGURE 6c. FIELD TEST CHART RECORDS.

APPENDIX A

Laboratory reports of SO_2 field samples from Crestlite Corporation, San Clemente, California, by EPA Method 6.

ANALYTICAL RESEARCH LABORATORIES, INC.

Lab/Storage Log Number

56056

Material/Sample Identity

IRC - Cotton/Rayon/Per samples, 7 runs, 14 samples

Date Received

5/17/76

P.O. or R.F. Number

Requested by

Wayne Perkins

Work Order

5141-01

Sample Disposition

( ) Retain ( ) Return (X) Destroy

Date Due

5/24/76

Ship To

Wayne Perkins
2700 DuPont Drive
Irvine, CA 92715

Invoice to

International Biophysics
(same address)
Attn: Mr. Mike Turner

SO_2 NO_2 content, ppm

Laboratory Report

	SO_2	NO_2
Test #2	6.7	276.
Test #3	13	242.
Test #4	9.5	225.
Test #5	8.6	176.
Test #6	69.	221.
Test #7	28.	262.
Test #8	44.	316.

RLP | 5/20/76

ANALYTICAL RESEARCH LABORATORIES, INC.

Lab/Shipper Log Number 56039

Material/Sample Identity: IBC Calcasieu, Inc. /Method 8 Impingers

Date Received: 5/14/76

P.O. or R.F. Number: Verbal

Requested By: Mr. Wayne E. Perkins

Work Order: 5141-01

Sample Disposition: ☐ Retain ☐ Return ☐ Destroy

Copies to Harvey

Date Done: 5/14/76

Ship To:

IBC/Calcasieu, Inc.
2700 DuPont Drive
Irvine, Ca. 92664

Subject of Work and Laboratory Services

Sulfuric Acid and SO_2

Nature of Laboratory Report

Q.C. Level: 1

Blanks were nil for the peroxide and isopropanol solutions.

Impinger #1

Total H_2SO_4 received: 130 mg. as H_2SO_4
113 mg. as SO_3
41 ppm H_2SO_4 or SO_3

Impinger #2

Total SO_2 received: 551 mg. or 0.0101 lb^3 @ STP, or
172 ppm based on 29.45 ft^3 gas at 32°C

PF | 5/13/76 | [illegible] | 64.10

Chemist and Date Signed